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(19)

(54) ELECTRIC ACCUMULATORS HAVING TEMPERATURE INDICATING MEANS

(71) We, VARTA BATTERIE AKTIENGESELLSCHAFT, a German Company, of Stöckener Str. 351, 3000 Hannover, Germany, do hereby declare the

invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The invention relates to electric accumulators having temperature indicating means.

In various operating phases, there occurs a change of temperature which may be used, for example, for controlling charging processes or which may serve as a means for monitoring the accumulator or functional parts of the accumulator.

In lead-acid traction batteries for battery-driven electric road vehicles, it may, for example, be advantageous to provide means for monitoring the temperature, particularly during the charging process, since, when the temperature of the cells is already at a high level as a result of a previous discharge, that temperature may easily further rise, during subsequent charging, to a level exceeding the maximum permissible temperature.

In alkaline accumulators, the temperature of the individual cells is advantageously also monitored during charging, since the capacity drops, for example, when the charging proceeds at excessive temperatures. In gas-tight alkaline accumulators, the charging with constant voltage necessitates a monitoring of the temperature, since an increase of the charge current and a continuously increasing temperature may result in a destruction of the cell (run-away effect).

In accumulators which are used for starting motors or engines; for example, in starter batteries, it may be advisable for the temperature to be monitored in order to obtain at excessively low temperatures an indication of the fact that an adequate cold start performance is not available and a signal initiating preheating of the accumulator may be emitted.

The operation of an accumulator may also be monitored by monitoring the temperature of so-called catalyst stoppers. In electric accumulators, and particularly in lead accumulators, hydrogen-oxygen mixtures are formed by electrolysis upon charging, discharge and storage, and the resulting loss of water has to be compensated by adding water at predetermined maintenance intervals. In the development of substantially maintenance-free accumulators it has in many cases become a practice to use recombining devices in which the hydrogen and oxygen evolved are recombined and then returned to the accumulator. Such recombining devices, which comprise an oxidation catalyst, are mounted above the individual cells of an accumulator battery in the form, for example, of so-called catalyst stoppers. Common catalyst recombining reactors are also used for recombing the gases of a number of accumulator cells.

The heat generated during the catalytic recombination process is dissipated to the outside and, in the construction of such recombing devices, particularly of catalyst stoppers, care has to be taken that the capacity of the materials to withstand thermal stresses is not exceeded. The outer casing, which generally serves as a condenser surface, has to be so dimensioned as to ensure that it does not reach a temperature of 100°C at maximum capacity or at peak output so that condensation is still possible.

The casing will generally be so designed as to ensure an operating temperature in the range 50° to less than 100° C.

A temperature monitoring element is particularly suitable for monitoring the functioning of the recombining stopper or of a common recombining reactor. However, in larger batteries which are in stationary operation or in operation in a vehicle this is a cumbersome and time-consuming method when

using the previously-known monitoring elements, particularly when the battery is accommodated in a restricted space. The scanning of the temperature of individual cells through electric structural elements, for example through thermoelements or thermocouples, tends to increase the cost; moreover, the multitude of individual cells and an electric circuit of this kind are potential sources of faults.

It is therefore an object of the invention to provide the simplest possible means for monitoring the temperature of an accumulator, of the individual cells of an accumulator or of component parts, particularly a catalyst stopper, of an accumulator.

According to the invention, there is provided an accumulator having visible means for indicating that a predetermined temperature, differing from the ambient temperature, has been attained, the visible means being responsive to the temperature of the accumulator or part of the accumulator and comprising a single substance which, at the predetermined temperature, changes its colour, colour intensity, luminescence or phosphorescence, this change being reversed when the temperature returns from the predetermined temperature towards the ambient temperature.

A dye may be provided, for example, on the housing or on the cover of an accumulator; however, the dye may also be provided on the terminal pillar of a cell, since a terminal pillar is a better heat conductor than are accumulator casings which are generally made of a synthetic resin. Alternatively the dye may be homogeneously mixed with the material of which the accumulator housing is made.

The dye may also be provided on the housing of a catalyst stopper, it being possible for the dye to be homogeneously admixed with the material of which the housing of the catalyst stopper is made.

It is known that organic and inorganic dyes suddenly change their optical properties when a determined temperature is reached. Thus, for example, some substances suddenly change colour at a determined temperature. These substances include particularly cobalt and nickel salts and zinc oxide and lead compounds. Thus for example, at a temperature of 75°C, $Co(NO_3)_2 . 2C_6H_{12}N_4 . 10 H_2O$ changes its colour reversibly from red to purple. The colour of lead iodide (PbI_2) changes from yellow to read at 130°C and the colour of zinc oxide changes from white to yellow upon heating. This colour change effect is utilised for measuring the temperature of so-called thermocolour dyes (see H. Lindorf, Technische Temperaturmessungen, Essen 1968, pages 158/159).

It will be understood that the change in colour is the most striking phenomenon; however, changes in the colour intensity may also be used for measuring temperature, particularly when the colour intensity changes suddenly. The known thermoluminescence of certain inorganic phosphorescent substances may be utilised in accordance with the invention. Upon irradiation; for example, with day-light; electrons in the semi-conductive crystal are excited and captured at positions of adhesion. Part of the irradiated energy is thus stored. When the crystal is heated to a temperature exceeding a determined characteristic temperature, the electrons are released from their positions of adhesion by thermal excitation and release their energy by emission of photons with resulting characteristic luminescence of the crystal. When a determined temperature is exceeded, it may also happen that the fluorescence of alkali halides is extinguished. There is also a substantial number of organic molecules which exhibit the phenomen of change of luminescence or phosphorescence at [a determined temperature.

Upon application of the aforedescribed principle of monitoring the temperature, and particularly of monitoring the functioning of catalyst stoppers, it is possible as hereinbefore mentioned, to provide a dye on the housing of a catalyst stopper and also, on the catalyst support as well. Since the operating temperature of the catalyst support is higher than that of the housing, other dye substances than that used for the catalyst housing have to be used for the support. In this example, the dyes may be applied by various methods. For example, where a transparent housing and a porous catalyst support are used, the pores of the support may be impregnated with the dye with the aid of a solvent. However, the dye may also be embedded in a lacquer or varnish-like mass which is then spread over the support to cover it wholly or partially with a figurative or abstract symbol. Both methods may also be applied to the outer casing of the stopper serving as a condenser surface. In stopper housings produced from a synthetic resin by plastic deformation, the dye is advantageously embedded in the pulverulent or granulated synthetic resin. Particularly useful results may be obtained by combining the heat-changeable dye with another, unchangeable dye of the same colour, so that two juxtaposed surface areas may form a figurative or abstract configuration. The eye, which responds particularly to comparison, thus readily detects the functioning indicated by the change in colour.

It will be understood that the dye may also be applied to any other surface of the stopper which is disposed in the path of the thermal flux between the catalyst and the exterior of the stopper and the temperature of which rises during the recombination process. These basic applications in a suitably modified form, are also suitable for monitoring the temperature of actual accumulator by application of the dye,

or introduction of the dye into, the accumulator housing or to or into the outside or inside of the accumulator cover. Suitable liquid crystals may also be used for indicating the temperature change.

Where fluorescent or phosphorescent substances are used, particularly good results may be obtained by irradiation with light from a lamp, which comprises a high proportion of ultraviolet wavelength. This is particularly effective in a battery with a very large number of individual cells, because anomalous cells are thus immediately manifest to the eye of the supervisory personnel so that the condition of such cells may be checked.

A starter battery provided with a catalyst stopper is hereinafter described with reference to a few examples.

The accompanying drawing shows the basic arrangement of such catalyst stoppers 4 in the starter battery. The temperature-indicating substance, particularly a dye, is provided in the form of a ring 5, on the housings of the catalyst stoppers.

Example 1

A mass of palladium-plated aluminium oxide granules which had been made water-repellent, served as catalyst. The aluminium oxide granules were disposed in a ceramic tube which had previously been impregnated with a lead iodide solution and had then been dried. The outer casing of the stopper was made of clear, transparent material such as that sold under the Registered Trade Mark "Plexiglass". The stopper was a cylindrical body, 40 mm. in height and 25 mm. in diameter. When the stopper was mounted above the cell of a starter battery, it was heated upon the occurrence of overcharge current. The occurrence of the overcharge current was indicated by the sudden change of colour of the ceramic tube from yellow to red. This phenomenon was visible from far off.

Example 2

The compound $Co(NO_3)_2 . 2 C_6H_{12}N_4 . 10 H_2O$ was applied with the aid of an alcoholic solution to the outer casing of the stopper described in Example 1. During operation, the colour changed from bright-red to purple.

Example 3

Aerosil (Registered Trade Mark) was impregnated with an aqueous solution of mercury iodide and potassium iodide. The surplus was poured off. A silver nitrate solution was then added slowly whereby a precipitate $Ag_2[HgI_4]$ was formed which was washed, filtered and dried. The powder thus obtained was admixed with polyethylene powder and the mixture was thermoplastically moulded in known manner to produce the housing of a stopper. A coil of blue asbestos cloth catalysed with paddadium and made water-repellent in material, e.g. polytetrafluorothylene, such as that sold under Registered Trade Mark "Teflon" and enclosed by a second coil of blue asbestos cloth impregnated with copper oxide and made water-repellent in Teflon was introduced into the interior of the housing. The stopper so produced was mounted above the cell of a lead accumulator. Upon evolution of gas during the overcharge phase, the colour of the yellow housing changed suddenly to bright red which was an indication that the change-over temperature of 45°C had been exceeded.

Example 4

Instead of using the dye $Ag_2[HgI_4]$ mentioned in Example 3, the corresponding copper salt $Cu_2[HgI_4]$ which at 67°C. changes suddenly from cherry red to brown, was used.

Example 5

Instead of using the dyes of the two preceding examples the compound $AgCu[HgI_4]$, which changes colour from yellow to orange at 35°C. and from orange to red at 40°C., was used.

With the arrangement in accordance with the present invention it is possible to monitor the temperature by very simple means without requiring any additional structural parts and circuits and thus at insignificant additional cost. This is of particular importance in multicell batteries, in which a conventional monitoring of each individual cell involves very high costs.

As hereinbefore mentioned, the temperature-indicating substance may alternatively be provided on the housing 1, the cover 2, or terminal pillar 3.

WHAT WE CLAIM IS:-

1. An accumulator having visible means for indicating that a predetermined temperature, differing from the ambient temperature, has been attained, the visible means being responsive to the temperature of the accumulator or part of the accumulator and comprising a single substance which, at the predetermined temperature, changes its colour, colour intensity, luminescence or phosphorescence, this change being reversed when the temperature returns from the predetermined temperature towards the ambient temperature.

2. An accumulator according to Claim 1, in which said substance is a dye which is provided on the housing of the accumulator.

3. An accumulator according to Claim 1, in which said substance is a dye which is applied to a terminal pillar of the accumulator.

4. An accumulator according to Claim 1, in which said substance is a dye which is applied to the housing of a catalyst stopper associated with the accumulator.

5. An accumulator according to any one of Claims 1 to 3, in which said substance is a dye in the form of a figurative or abstract symbol which is applied to a surface of the accumulator.

6. An accumulator according to any one of Claims 2, 4 or 5 in which said substance is a dye which is admixed with the material from which

the housing is made.

7. An accumulator according to any one of Claims 1 to 6, in which said substance is lead iodide, silver-mercury iodide, silver-copper-mercury-iodide, or copper-mercury iodide.

8. An accumulator according to any one of Claims 1 to 6 in which the said substance comprises the compound $Co(No_3)_2 . 2C_6H_{12}N_4 . 10H_2O$.

9. An accumulator having temperature-indicating means substantially as described herein with reference to the accompanying drawing.

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1437752 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*